Yazaki, Y. and Collins, P.J. Provisional Patent Application PO09260 (1997)

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PROVISIONAL SPECIFICATION

Applicant:

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION

Invention Title:

HIGH YIELD TANNIN EXTRACTS

The invention is described in the following statement:

HIGH YIELD TANNIN EXTRACTS

The present invention relates generally to natural products and in particular to useful materials obtained from naturally occurring forest resources. More particularly, the present invention relates to tannin extracts from forest resources such as trees, barks, leaves and the like. Even more particularly, the present invention relates to improved methods of extracting tannins and to tannin extracts having improved properties, particularly properties which are useful in making adhesives that are particularly adapted for use in making reconstituted or synthetic wood products such as laminated timbers, chipboard, medium density fibreboard, plywood and the like. The present invention finds particular application in methods of extracting tannin from *Pinus radiata* bark, which tannin extracts have improved properties such as higher yields, higher quality, lower viscosity and more uniform properties, and using the extracts in formulating an adhesive for use in the manufacture of reconstituted wood products such as particle board, plywood, medium density fibreboard and the like.

Although the present invention will be described with particular reference to tannin extracts and methods of extracting tannin from *Pinus radiata* bark and the use of such extracts in adhesives in the manufacture of reconstituted wood products, it is to be noted that the scope of the present invention is not limited to the described embodiment but rather the scope of the present invention is more extensiv so as to include other methods of obtaining the extracts, extracts from other materials, and the use of the extracts in other applications.

Radiata pine (*Pinus radiata* D. Don) bark contains significant amounts of reactive tannins which can be useful in the manufacture of water-proof and durable wood adhesives, particularly for the manufacture of compressed synthetic wood products such as particleboard, medium density fibreboard, plywood and the like. It has been estimated that the existing amount of pine bark available could provide more than twice the amount of synthetic phenol-formaldehyde (PF) adhesives that are presently being used in the Australian reconstituted wood manufacturing industry.

Despite pine bark having great potential for commercialisation in the production of wood adhesives, there are a number of problems associated with the use of this material, such as, for example, low yields of tannins extracted from the bark, the tannin extracts having excessively high viscosity and being of variable quality, all of which in the past have prevented the commercial acceptance and industrial use of radiata pine bark extracts in Australia. Compounding the above-mentioned problems is the fact that the yield of tannin extracts extracted from the bark, as well as being low, also varies considerably between different batches of bark being treated, depending on the source of the bark, the conditions under which the bark has been stored, the method used in extracting the tannin and the actual extraction conditions employed in obtaining the extracts. Further, the yield is dependent on the temperature at which the extraction occurs, the particle size of the bark from which the tannins are extracted and also on the pH of the extracting solvent and slurry. Additionally, radiata pine bark tends to form relatively smaller sized particles during the grinding stage and, accordingly, the bark particles are relatively more tightly packed together during the filtration stage so that efficient filtration is difficult to achieve which, in turn, results in very low yields of tannin extract or excessively large amounts of solvent being used.

Another problem encountered in formulating wood adhesives containing tannin extracts from radiata pine bark stems from the excessively high viscosity of the tannin extract. As an example, the viscosity of a tannin extract obtained using an aqueous solvent at 100°C at 40% solids and a pH of 4 was found to be 18,000 mPa.s (cps). In this case, the tannin extract could not be formulated into any wood adhesive because of its excessive viscosity which precluded applying the formulated adhesive by conventional application techniques, such as by spraying or coating.

Although a number of different methods for reducing the viscosity of the tannin extracts have been tried in the past, including the most common method based on the treatment of tannin extracts with sodium sulphite or sodium metabisulphite (sulphitation), such methods have not been entirely successful for a variety of reasons, mainly concerned with the undesirable reduction of the different molecular weight fractions present in the extract, particularly the low molecular weight polymer fractions, which results in a skewed distribution of molecular weight fractions of the tannin extract towards the high to mid weight range due to the preferential breakdown of the lower molecular weight fractions. This undesirable distribution of molecular weight fractions contributes to the variability of the properties of the tannin extract and the adhesives formulated therefrom.

A still further problem relates to the variable quality of wood adhesives formulated using the radiata tannin extracts from radiata pine bark. Radiata pine bark contains polyflavanoids which are reactive with formaldehyde and non-reactive components, such as carbohydrates and polyphenols. The variable quality of adhesives is largely due to the amount and purity of the polyflavanoids in the tannin extracts and to the molecular weight distribution of the polyflavanoids. In the past, it has been difficult to control the amount of polyflavanoids and their molecular weight distribution which has led to

variable quality adhesives.

In the past, methods of addressing and/or overcoming the above indicated problems relating to excessively high viscosity and variable quality have been attempted. One such method has been to use ultrafiltration processes. However, such ultrafiltration processes are too expensive for the commercial production of wood adhesives from radiata pine bark. Another way of overcoming the problems has been to use diffusion-extraction technology or squeeze-extraction technology in which the bark particles are subject to high pressure or the like. However, both of these conventional extraction processes require the tannin extraction step to take place in two or more separate steps or stages which is both time consuming and expensive since the multiple steps result in the extracting equipment being used for long periods for repetitive steps with little throughput or production occurring. To date, all of these existing technologies and methods employing the conventional diffusion- and/or squeeze-extraction methods have not resulted in the production of commercially acceptable, high quality tannin extracts at an economical rate.

Thus, when all of the factors relating to extractive yield, excessively high viscosity and variable quality of tannin extracts are considered, it is clear that a completely new technology was needed to produce high quality wood adhesives that could be used with conventional reconstituted wood processing equipment and materials. This new technology has now been developed by the present inventors. Thus, it is an aim of the present invention to provide a method and apparatus which at least addresses the problems of existing methods and apparatus of producing tannin extracts for use in wood adhesives used in the reconstituted wood industry by providing an extracting method which offers high yield, lower viscosity and more uniform properties, which also takes less time to achieve. According to the present invention there is

provided a process of extracting tannin from a tannin-containing raw material comprising the steps of

providing a supply of suitably sized tannin-containing raw material,

contacting the tannin-containing material with a suitable extracting medium,

defibrating the mixture so formed, and

separating the defibrated tannin-containing material into a first fraction being a liquor containing the tannin extract obtained from the mixture and a second fraction being the residue of the tannin-containing material, thereby forming an extract of tannin from the tannin-containing raw material.

According to another aspect of the present invention there is provided a method of forming an adhesive for use in the manufacture of a reconstituted wood product, said method comprising formulating a tannin extract into the adhesive wherein the tannin extract is obtained by the method of the present invention.

According to another aspect of the present invention there is provided a method of making a reconstituted wood product or similar, comprising using an adhesive containing a tannin extract extracted in accordance with the method of the present invention.

According to a still further aspect of the present invention there is provided a tannin extract wherein the tannin extract is obtained using the method of the present invention.

According to a still further aspect of the present invention there is provided an adhesive suitable for use in the manufacture of a reconstituted wood product wherein said adhesive includes a tannin extract obtained in accordance with the method of the present invention.

According to a still further aspect of the present invention there is provided a reconstituted wood product made using an adhesive wherein the adhesive comprises a tannin extract obtained in accordance with the

method of the present invention.

Typically, the tannin-containing raw material is a forestry resource, such as timber, bark, leaves or the like. More typically, the tannin-containing material may be a softwood bark or a hardwood bark. Even more typically, the material is a bark such as, for example, pine bark, wattle bark, larch bark, spruce bark or the like.

The tannin of the present invention is typically a condensing tannin, typically obtained from a softwood bark, or a non-condensing tannin, typically obtained from a hardwood bark, such as from gum trees or similar.

Any suitable bark at any moisture content may be utilised, although, typically, green bark may be preferred, if long term storage is not required prior to extraction.

Any suitable age bark may be utilised, although, typically, the bark is either young bark, typically 15 to 20 years old, or is old bark, typically 35 or more years old, or a combination of two or more barks.

Typically, the method of the present invention involves repeated extraction using the same liquor so that the liquor is recycled through the bark a plurality of times to facilitate concentration of the tannin extract in the liquor thereby resulting in a higher concentration of tannin being produced.

Any suitable temperature may be utilised, although, typically, the extraction of the bark with the aqueous solvent is carried out at a temperature from room temperature up to 180°C or more. More typically, the temperature is up to 100°C. Even more typically, the temperature is from 20°C to 100°C.

Any suitable solvent and solvent to bark ratio may be employed, although, typically, the solvent used to form the slurry of bark is water. More typically, the aqueous slurry has a water to bark ratio of from 10:1, preferably from about 3:1 to 8:1, more preferably about 6:1.

Any suitable chemicals may be utilised at any

time to facilitate efficient extractions. Typically, such chemicals may be selected from the group comprising alkali metal hydroxides, wetting agents and hydrogen bond breakers, but this is by no means intended to imply that such chemicals for use in this extraction process are limited to these. Typically, the bark mixture with extracting medium is defibrated in one, two, three, four or more passes. Typically, each successive pass, if more than a single pass is used, may be at a decreasing gap setting, such as, for example, 0.5 mm, 0.05 mm, and substantially zero or similar. However, any suitable gap setting in any subsequent pass may be utilised.

Typically, the defibrator apparatus of the present invention is a refiner mechanical pulp (RMP) defibrator using either two counter-rotating discs or a single rotating disc against a stationary disc or even a revolving double-sided disc located between two stationary discs. More typically, chemicals are added to the refiner or defibrator to assist in breaking the bark down into individual fibres.

Typically, the method of the present invention includes further optional processing steps, such as, for example, comminuting the bark pieces to a more uniform distribution of sizes by a hammer-mill or similar equipment.

Typically, the tannin yield from radiata pine bark may be in the range of from 20% to 40%. Typically, the viscosity of the tannin extract is less than 1000 cps, more typically, less than 500 cps and preferably less than 200 cps after mild sulphitation, all measured at 25°C and a solids content of 40%.

The present invention will now be illustrated by examples and described with reference to the following example. It is to be noted that the scope of the present invention is not limited to the example but that the example is illustrative of the invention only.

Example 1

A sample of young bark, being of the order of 15 to 20 years old, was collected from CSR Timber Products in Oberon, NSW, a company involved in forestry and timber products, and a second sample of bark, being old bark having an age in excess of 35 years, was obtained from Boral Sawmill in Oberon, NSW, another company involved in the forestry and timber industry. The two samples of bark supplied by the two different de-barkers were hammer-milled to reduce the size of the pieces of bark to centimetre size pieces of a more or less uniform size distribution and then dried at 40°C for 24 hours for storage prior to extraction.

A sample of each of the barks equivalent to 100 g of oven dried bark was selected for subsequent processing. A slurry of each bark sample with water was formed at a water to bark ratio of 6:1. The slurry was heated, typically to 100°C. The bark slurry was then defibrated using a laboratory Bauer refiner and a No. 9 grinding disc in successive passes. The first pass was conducted at a gap setting of 0.50 mm using the 200 mm disc laboratory Bauer refiner. The second pass was conducted at 0.05 mm and the third pass at substantially 0 mm. Prior to the defibration process, the refiner was heated by pouring boiling water through the refiner until it became hot. During each pass of the slurry through the defibrator, extra boiling water was added for washing the defibrator. Usually the amount of water added resulted in about 3000 ml extract solution being produced for each pass.

The extracted slurry was then filtered through a cloth filter under vacuum to separate the liquor containing the tannin and the bark residue. However, it is to be noted that any suitable filter material or means or installation may be used such as squeeze-filtering. The bark residue was then dried for subsequent processing at 40°C and 25% relative humidity while the total solids of the liquor was determined to calculate th yield of tannin

extract and the liquor was then freeze-dried for Stiansy analysis, viscosity determination, sulphitation and gluing tests. The percentage of polyflavanoid yield in each extract was calculated by multiplying the percentage of extractive yield by the Stiansy value.

The extractive yields, Stiansy values, viscosities and gluing properties of the tannin extracts obtained using this new extraction method of the present invention are provided in Tables 1 and 2 in which Table 1 shows the results obtained using young bark from CSR and Table 2 shows the results of using old bark obtained from Boral.

As can readily be seen from the results provided in Tables 1 and 2, when the values of the various parameters relating to the tannin extract produced in accordance with the method of the present invention are compared to the values of similar parameters using conventional diffusion-extraction and squeeze-extraction methods, several advantageous characteristics of the tannin extracts produced in accordance with the present invention are readily apparent.

When the various values of the extractive yield of each of the three samples are compared, it can be seen that in the case of the CSR young bark (Table 1), using the method of the present invention there is 30.4% extraction as compared to 20.5% using the diffusion-extraction method and 22.0% using the squeeze-extraction method. When the Boral old bark sample is considered (Table 2), there is a similar increase in extractive yield in that 32.4% is extracted using the process of the present invention as compared to 26-28% using the CSR diffusion-extraction method and 25.4% using the squeeze-extraction method. The Stiansy percentage provides an indication of the quality of the tannin extract and gives an indication of the amount of polyflavanoid present in the extract. As can be seen from Table 1, using the method of the present invention 81.2% is obtained, whereas both conventional methods produce 49.7%

and 47.2% on the one hand, and 56.9% and 55.7% on the other hand, both significantly below that obtained using the method of the present invention.

With respect to Table 2, 86.7% was obtained using the method of the present invention as compared to 73.0% and 73.2% using the diffusion-extraction method, and 72.7% and 68.6% using the squeeze-extraction method. The reason for the two sets of values for the conventional extraction techniques is that there were two levels of sulphitation, being 5% and 10%, to reduce the viscosity, whereas with the method of the present invention only a 5% level of sulphitation was required.

There is a single stage extraction required in the present invention whereas both prior art methods require at least a two stage extraction.

Low levels of sulphitation are required as indicated by 5% for the method of the present invention as compared to 5% and 10% required for conventional processes.

The viscosity of the tannin extract obtained in accordance with the present invention as indicated in Table 1 is 107-135 cps, whereas the viscosities of the various samples of the extracts obtained using the conventional methods for low and high sulphitation respectively were 2220-7090 and 1200-4070 using the diffusion-extraction method and 2930-6910 and 829-3460 using the squeeze-extraction method. Clearly, there is a significant decrease in the viscosity of the tannin extract obtained by the method of the present invention.

Similarly, when the viscosities of the sample of Table 2 are considered, the extract of the present invention has a viscosity of 126-153 cps as compared to the low and high sulphitation viscosities of 984-2580 and 520-1670 respectively using the diffusion-extraction method, and 890-1000 and 414-506 respectively using the squeeze-extraction method. Again, this demonstrates a considerable reduction in viscosity using the method of the present invention as compared to conventional extraction methods.

When the values in Tables 1 and 2 relating to the strengths of the glue bond are considered, it is clear that the adhesive formulated using the tannin extract method of the present invention resulted in a much stronger bond than using the tannin extracts obtained by conventional techniques. It is pointed out that the value of wood failure in Tables 1 and 2 refers to the percentage of wood product which degrades in preference to the glue failing. A high value of wood failure indicates a very strong adhesive bond since the wood degraded to a large extent whilst the adhesive was substantially intact, whereas a low rate of wood failure represents a very weak adhesive bond since the adhesive fails before the wood has a chance to degrade. As can be readily seen from the values of Tables 1 and 2, the wood failed in preference to the adhesive bond when using adhesives incorporating tannin extracts obtained from in the method of the present invention, whereas when conventional methods were used to extract the tannins the adhesives made from these extracts exhibited failure in the glue bond rather than the wood degrading. This clearly demonstrates the superiority of the tannin extract produced by the method of the present invention in formulating suitable adhesives.

Advantages of the present invention include the following:

- The simplified process of the present invention involves a single extraction stage only, as compared to the plurality of steps of conventional methods.
- A higher yield tannin extract is obtained with a lower viscosity and more uniform properties.
- The extracted residues remaining after the tannin extracts have been removed can be used as a source of fibres for the manufacture of MDF which is a value-added product selling at a premium price. Thus, not only is the tannin extract useful as one component in wood adhesives, but

also the bark residue is useful as a source of fibres for the manufacture of MDF, and both will make bark a very valuable and sought-after resource.

The described arrangement has been advanced by explanation and many modifications may be made without departing from the spirit and scope of the invention which includes every novel feature and novel combination of features hereindisclosed.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is understood that the invention includes all such variations and modifications which fall within the spirit and scope.

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Table 1. Comparison of CSR Diffusion and CSIRO Squeeze extractions with CSIRO Defibration extraction

CSR Young Bark

	CSR Diffusion		CSIRO Squeeze		Defibration
Bark No.	153 + 154		CS16		Not specified
Bark crushing	Hammer-milled		Hammer-milled		Hammer-milled
Bark grinding	Wiley-milled		Wiley-milled		None
Bark particle size (mm)	<12.5		<12.5		variable
Extraction stage	Two stages		Two stages		One stage
Extractives yield	20.5%		22.0%		30.4%
Sulphitation	5%	10%	5%	10%	5%
Stiasny (%)	49.7%	47.2%	56.9%	55.7%	81.2%
Viscosity (mPa.s at 25C)	2220-7090	1200-4070	2930-6910	829-3460	107-135
Glued product	Plywood	Plywood	Plywood	Plywood	Plywood
Wood failure (%) Dry	0%	5%	20%	20%	80%
Wood failure (%) Wet	Not available		Not available		73%

Table 2. Comparison of CSR Diffusion and CSIRO Squeeze extractions with CSIRO Defibration extraction

Boral Old Bark

	CSR Diffusion		CSIRO Squeeze		Defibration
Bark No.	157+159	158+160	CS17		Not specified
Bark crushing	Hammer-milled		Hammer-milled		Hammer-milled
Bark grinding	Wiley-milled		Wiley-milled		None
Bark particle size (mm)	<12.5		<12.5		Variable
Extraction stage	Two stages		Two stages		One stage
Extractives yield (%)	26.0%	26.0%	25.4%	25.4%	32.4%
Sulphitation	5%	10%	5%	10%	5%
Stiasny value (%)	73.0%	73.2%	72.7%	68.6%	88.7%
Viscosity (mPa.s at 25C)	984-2580	520-1670	880-1000	414-506	126-153
Glued product	Plywood	Plywood	Plywood	Plywood	Plywood
Wood failure (%) Dry	35%	50%	35%	70%	95%
Wood failure (%) Wet	Not available		Not available		75%